

CARBON MAPPING AND CARBON-XANES MEASUREMENTS ON CARBONATE GLOBULES FROM AH84001: G. J. Flynn¹, L. P. Keller², J. Kirz³, S. Wirick³, S. Bajt⁴ and H. N. Chapman³, 1) Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY 12901, 2) MVA Inc., 5500-200 Oakbrook Parkway, Norcross, GA 30093, 3) Dept. of Physics, SUNY-Stony Brook, Stony Brook, NY 11794, 4) The University of Chicago, Chicago, IL 60637.

McKay et al.¹ have reported possible evidence for ancient biological activity in carbonate globules and the rims on the carbonate globules from the AH84001 meteorite, believed to be from Mars. Using laser ionization mass spectrometry, they found low bulk concentrations (>1 ppm) of polycyclic aromatic hydrocarbons (PAHs), and report "the PAHs were found in the highest concentrations in the regions rich in carbonates."¹ Since PAHs are frequently formed by the degradation of living organisms, the presence of PAHs was interpreted as one possible indicator of ancient biological activity associated with the carbonates. The laser ionization mass spectrometer instrument used for the PAH measurement has extremely good sensitivity but relatively poor spatial resolution, a 50 micron beamspot which is roughly comparable with the size of the individual carbonate globules and significantly larger than the thickness of the rims.

The Scanning Transmission X-Ray Microscope (STXM), installed on beamline X1A of the National Synchrotron Light Source, has previously been employed to map the distribution of carbon and to determine the bonding states (i.e. to infer the molecular properties of the carbon-bearing phases) of 10 micron interplanetary dust particles.² The STXM has extremely good spatial resolution (beamspot <50 nanometers in diameter) but significantly poorer sensitivity (~1% carbon) than the laser ionization mass spectrometer. If the PAHs found in association with the AH84001 carbonates are concentrated in the rims or some minor phase within the carbonates, their local concentrations might exceed the detection limit of the STXM.

The bulk of the carbon in both the carbonate globules and the rims is expected to be bound in carbonates. Our prior work on interplanetary dust demonstrates that there is a strong chemical shift for the C-O bond in carbonates resulting in a peak in the C-XANES absorption spectrum at a significantly higher energy than that found for PAHs, graphite and other carbon-ring structures as well as most phases with C-C, C=C, or C-H bonds. The C-XANES spectra of graphite, and two PAHs (pyrene and dibenzoperylene) show strong absorptions in the region between 284 eV and 287 eV while Ca-carbonate shows an absorption peak at ~290 eV but no absorption in the 284 to 287 eV energy range [see Figure 1]. Because the carbonate has no absorption near 285 eV, small amounts of PAHs, graphite or other carbon phases which absorb strongly near 285 eV should be detectable in a carbonate matrix. If so, the STXM could be used to map the distribution of non-carbonate carbon and to determine the bonding state(s) of this carbon.

A fragment of a carbonate globule, including rim material, from AH84001 was imbedded in elemental sulfur, an ultramicrotome thin section (~200 nanometers thick) was prepared, deposited on an SiO substrate, and examined with the STXM. The use of S as the imbedding medium and SiO as the substrate eliminates carbon contamination from the traditional organic imbedding media and carbon substrates. The section was mapped, with a beam spot ~50 nanometers in diameter, at three energies: ~280 eV (an energy where carbon has essentially no absorption), ~285 eV (an energy where PAHs and graphite absorb strongly but carbonate does not absorb), and ~300 eV (an energy where all forms of carbon absorb strongly). At each pixel, the ratio of the absorption at 300 eV to 280 eV is proportional to the local abundance of carbon in the thin section. The carbon absorption was relatively constant over the entire sample, indicating a relatively homogeneous carbon distribution. However, the ratio of the absorption at ~285 eV to that at ~280 eV, which maps the distribution of only those carbon compounds which absorb strongly near 285 eV, showed an inhomogeneous distribution, indicating that, in some regions of the sample, a second carbon-bearing phase was present.

Carbon-XANES spectra were taken at two spots on the sample. The spectrum taken where the carbon map showed no significant absorption at ~285 eV is consistent with the carbon at that spot being bound in carbonate. However, the spectrum taken at a spot where the map showed a significant ~285 eV absorption shows a sharp peak near 285 eV consistent with the absorption from PAHs, graphite or other C-C, C=C, or C-H bonds, as well as an absorption feature consistent with carbonate. These results demonstrate that this section of an AH84001 carbonate globule contains two distinct carbon-bearing phases:

- 1) a carbonate, which is distributed relatively homogeneously, and,
- 2) a carbon-bearing phase with an absorption peak near 285 eV, which is distributed inhomogeneously.

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Further experiments are in progress to correlate the location of the non-carbonate carbon regions with TEM images of the section, to eliminate the possibility of sample contamination, and to identify the second carbon-bearing phase in the carbonate globule. The STXM, because of its high spatial resolution, provides carbon measurements which are complimentary to those from the laser ionization mass spectrometer, which has much poorer spatial resolution but greater sensitivity.

These results demonstrate that the STXM can be used to detect non-carbonate carbon in the globules from AH84001, to map the distributions of carbon bound in carbonates and non-carbonate carbon in these samples, and, possibly, to identify the non-carbonate carbon-bearing phase in these carbonate globules.

References:

- 1) McKay, D. S., E. K. Gibson, K. L. Thomas-Keprta, H. Vali, C. S. Romanek, S. J. Clemett, X. Chiller, C. R. Maechling, and R. N. Zare, *Science*, 273, 924ff (1996)
- 2) Bajt, S., H. Chapman, G. J. Flynn, and L. P. Keller, *Lunar & Planetary Science XXVII*, 57-58 (1996)

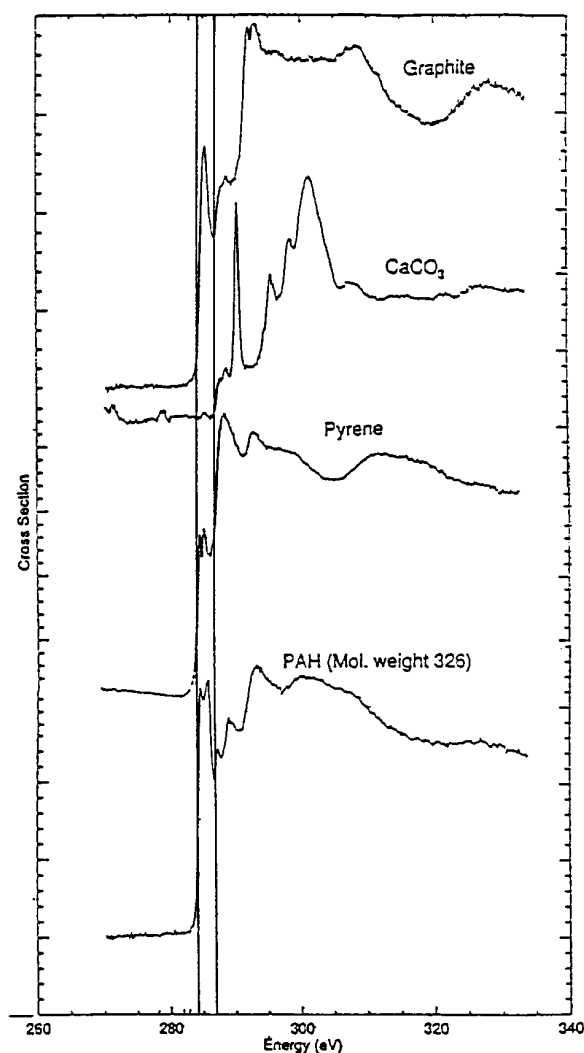


Figure 1: C-XANES spectra showing the absorption cross-sections (arbitrary units) for graphite, calcium carbonate (CaCO_3), and two PAHs, pyrene (molecular weight 202) and dibenzoperylene (molecular weight 326), versus incident X-Ray energy taken with the STXM. The vertical lines highlight the region from 285 to 287 eV, where graphite and the two PAHs have a strong absorption, but the carbonate absorption is shifted to a higher energy (~290 eV).